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RELATIONS FOR THE THERMODYNAMIC AND  
TRANSPORT PROPERTIES IN THE TESTING  
ENVIRONMENT OF THE LANGLEY  
HYPERSONIC  $CF_4$  TUNNEL

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## SUMMARY

Relations for the thermodynamic and transport properties for gaseous  $\text{CF}_4$  are presented that can be used in flow-field computer codes and theoretical analyses for comparison of results with experimental data from the Langley Hypersonic  $\text{CF}_4$  Tunnel. The thermodynamic relations are based on a thermally perfect but calorifically imperfect gas. These relations are adequate for the testing environment of the  $\text{CF}_4$  Tunnel and are simpler to use than the imperfect gas relations required to define the complete expansion from the tunnel reservoir.

The relations for the transport properties are based on the kinetic theory of gases in which published experimental data are used in the derivation of the relations. Extensive experimental data were located for viscosity and the derived relation should provide values for viscosity with errors of less than 1 percent. The experimental data for thermal conductivity were limited with significant disagreement between the various sources. Based on the limited experimental data, the derived relation will probably provide values for the thermal conductivity with errors of no more than 5 percent which is within the accuracy of the experimental data.

## INTRODUCTION

The Langley Hypersonic  $\text{CF}_4$  Tunnel is a conventional-type, blow-down, wind tunnel that uses carbon tetrafluoride ( $\text{CF}_4$ ) as the test gas. A description and summary of test conditions for this tunnel are given in reference 1. The flow is nominally a Mach number 6 with a normal-shock, density ratio of about 12. As discussed in reference 2, the basic concept for the  $\text{CF}_4$  Tunnel is to provide a conventional-type, wind tunnel to simulate real-gas effects that occur for actual hypervelocity flight. In hypervelocity flight, shock density ratios of 10 to 20

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may be encountered and values of 1.1 are approached for the ratio of specific heats due to chemical dissociation of the high-temperature gas behind a shock wave. In conventional wind tunnels the test gas does not dissociate. Those tunnels that use air or nitrogen as the test gas are limited to a ratio of the specific heats of 1.4 and a density ratio approaching 6. Tunnels that use helium are limited to a ratio of specific heats of 1.67 and a density ratio of 4. The use of  $\text{CF}_4$  as the test gas in a conventional wind tunnel provides a test environment with a shock density ratio of 12 and thus better simulates the flow environment over a hypervelocity vehicle.

The relations for the thermodynamic and transport properties of  $\text{CF}_4$  used to predict the flow conditions in the Langley Hypersonic  $\text{CF}_4$  Tunnel are those presented in references 3 and 4. The thermodynamic relations are based on an imperfect equation of state, intermolecular force effects are accounted for, and high-pressure effects are included for the transport properties. This detailed treatment is necessary because of the high pressures existing in the reservoir and beginning expansion region of the nozzle. However, at the test section (testing environment) the gas has expanded to such low-pressure conditions in both the free stream and behind a normal shock that imperfect gas effects are negligible on the thermodynamic properties and high-pressure effects can be neglected for the transport properties. The testing environment for the  $\text{CF}_4$  Tunnel (see ref. 1) is in the range of 0.2 to 22  $\text{kN/m}^2$  for pressure and 150 to 800 K for temperature. The lowest values of pressure and temperature are those in the free stream at the lowest reservoir settings and the largest values refer to conditions behind a normal shock at the highest reservoir settings. For these conditions the  $\text{CF}_4$  gas can be treated as thermally perfect with a compressibility factor equal to 1 and calorifically imperfect with specific heats given as a function only of temperature. Therefore, in the testing environment of the  $\text{CF}_4$  Tunnel, the full detailed relations presented

in references 3 and 4 to account for high-pressure effects on the thermodynamic and transport properties of  $\text{CF}_4$  are not needed and simpler relations can be used in analyses for comparisons with the experimental results.

The relations used in references 3 and 4 for the transport properties of  $\text{CF}_4$  are based on the work of reference 5 in which the equations for viscosity and thermal conductivity are curve fits of experimental data. The experimental data used covered only a temperature range of approximately 230 to 460 K; thus, extrapolations of the curve fits are necessary to define the transport properties over the complete range of the testing environment in the  $\text{CF}_4$  Tunnel.

The purpose of the present technical memorandum is to develop and present relations for the thermodynamic and transport properties for gaseous  $\text{CF}_4$  that can be used in flow-field computer codes and theoretical analyses for comparison of results with the experimental data from the Langley Hypersonic  $\text{CF}_4$  Tunnel. The intent is to provide relations that are valid for the testing environment of the  $\text{CF}_4$  Tunnel and yet be easier to use than the detailed relations presented in references 3 and 4. The thermodynamic properties are based on a thermally perfect but calorifically imperfect gas. For the transport properties, a literature search was conducted for experimental data and these data were interpreted in terms of the Kinetic theory of gases.

#### SYMBOLS

$A_n$	constants in equation (7), values defined by equation (8)
$a$	speed of sound, m/s
$B_n$	constants in equation (17), values defined by equation (18)
$c_p$	specific heat at constant pressure, J/kg-K
$c_v$	specific heat at constant volume, J/kg-K
$D$	diffusion coefficient, $\text{m}^2/\text{s}$
$g_i$	statistical weights

$h$	enthalpy, J/kg
$k$	thermal conductivity, w/m-k
$M$	molecular weight for $CF_4$ , 0.088005 kg/mole
$N_{Pr}$	Prandtl number, $\mu c_p/k$
$p$	pressure, $N/m^2$
$R$	gas constant for $CF_4$ , 94.475 J/kg-K
$s$	entropy, J/kg-K
$T$	temperature, K
$T_\epsilon$	maximum energy of attraction in temperature units, K
$T^*$	reduced temperature, $T/T_\epsilon$
$u$	internal energy, J/kg
$x_i$	quantity defined by equation (6)
$z$	rotational collision number
$\gamma$	ratio of specific heats, $c_p/c_v$
$\delta$	quantity defined by equation (41)
$\theta_{v_i}$	vibrational energies in temperature units, K
$\mu$	viscosity, $N\cdot s/m^2$
$\rho$	density, $kg/m^3$
$\sigma$	collision diameter, m
$\Omega(2,2)$	reduced collision integral

#### Superscripts

$r$	rotational energy
$t$	translational energy
$v$	vibrational energy

#### Subscript

$t$	refers to values from $CF_4$ Tunnel, see equations (24) and (25)
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## THERMODYNAMIC PROPERTIES

The thermodynamic properties for  $\text{CF}_4$  are based on a thermally perfect, calorifically imperfect gas. The calorifically imperfect nature of the gas is due to the vibrational modes which are not fully excited for the temperatures of interest. The thermally perfect, equation of state is

$$p = \rho RT \quad (1)$$

where

$$R = 94.475 \text{ J/kg-K} \quad (2)$$

for  $\text{CF}_4$  based on a molecular weight of 0.088005 kg/mole.

Equations for the specific heat at constant pressure, enthalpy, and entropy are presented in several forms for each property. A particular form might be more useful than another depending on the application. The reference states must be known in comparing the enthalpy and entropy between different sources. In the present work, the reference states are that the enthalpy and entropy are zero at a reference temperature of 0 K and a reference pressure of  $101325 \text{ N/m}^2$  (1 atmosphere). By this definition, the heat of formation is neglected in the enthalpy. The heat of formation does not need to be included in the enthalpy because  $\text{CF}_4$  will not dissociate at any condition for the  $\text{CF}_4$  Tunnel. As a point of interest, reference 6 gives the heat of formation for  $\text{CF}_4$  at 0 K as  $-10.536 \text{ MJ/kg}$ . This value could be added to the enthalpy if one wanted to include the heat of formation in the definition for enthalpy.

The properties of specific heat at constant pressure, enthalpy, and entropy can be calculated by statistical thermodynamics. The relations given in the JANAF tables, reference 6, for a nonlinear polyatomic molecule treated as a rigid rotor and harmonic oscillator, with anharmonic corrections neglected, can be used to express the properties for  $\text{CF}_4$  as

$$\frac{c_p}{R} = 4 + \sum_{i=1}^4 \frac{g_i x_i^2 \exp(-x_i)}{[1 - \exp(-x_i)]^2} \quad (3)$$

$$\frac{h}{RT} = 4 + \sum_{i=1}^4 \frac{g_i x_i \exp(-x_i)}{[1 - \exp(-x_i)]} \quad (4)$$

$$\frac{s}{R} = 18.60 + 4 \ln(T) - \ln(p) + \sum_{i=1}^4 g_i \left\{ \frac{x_i \exp(-x_i)}{[1 - \exp(-x_i)]} - \ln[1 - \exp(-x_i)] \right\} \quad (5)$$

where

$$x_i = \frac{\theta_{v,i}}{T} \quad (6)$$

The vibrational energy ( $\theta_v$ ) expressed in temperature units and the statistical weight ( $g$ ) for each of the four vibrational modes of  $CF_4$  are:

<u>i</u>	<u><math>\theta_{v,i}</math>, K.</u>	<u><math>g_i</math></u>
1	1307	1
2	626	2
3	1846	3
4	909	3

Equations (3) to (6) were derived from the general expressions given in the JANAF tables, except for the addition of the pressure term in the equation for entropy, using the spectroscopic constants listed in the JANAF tables for  $CF_4$ . Thus, values calculated with these equations will agree exactly with the tabulated values for  $CF_4$  listed in the JANAF tables.



Relations were also determined for  $c_p$ ,  $h$ , and  $s$  based on a sixth degree polynomial curve fit for  $c_p$  over the temperature range of 100 K to 900 K from results calculated using the statistical thermodynamic equation. This temperature range is sufficient for the testing environment for the  $CF_4$  Tunnel. The curve fit for  $c_p$  is

$$\frac{c_p}{R} = \sum_{n=1}^7 A_n T^{(n-1)} \quad (7)$$

where

$$\left. \begin{aligned} A_1 &= 4.1224 \\ A_2 &= -1.5035 \times 10^{-2} \\ A_3 &= 2.0719 \times 10^{-4} \\ A_4 &= -6.1972 \times 10^{-7} \\ A_5 &= 9.0130 \times 10^{-10} \\ A_6 &= -6.5865 \times 10^{-13} \\ A_7 &= 1.9308 \times 10^{-16} \end{aligned} \right\} \quad (8)$$

Using

$$dh = c_p dT \quad (9)$$

and equation (7) for  $c_p$ , the enthalpy can be expressed as

$$\frac{h}{R} = 10.377 + \sum_{n=1}^7 \frac{A_n}{n} T^n \quad (10)$$

The differential expression for entropy is

$$T ds = dh - \frac{dp}{\rho} \quad (11)$$

Using equations (7), (9), and (11) and the equation of state (eq. (1)), the entropy can be expressed as

$$\frac{s}{R} = 18.723 + A_1 \ln(T) - \ln(p) + \sum_{n=2}^7 \frac{A_n}{(n-1)} T^{(n-1)} \quad (12)$$

The values for the properties at 100 K necessary to integrate the relations to derive equations (10) and (12) were taken from the statistical thermodynamic results. Over the temperature range of 100 K to 900 K, the maximum errors are 0.57 percent for  $c_p$ , 0.11 percent for  $h$ , and 0.02 percent for  $s$  when compared with values calculated by the statistical thermodynamic equations.

Other thermodynamic properties can be calculated from the known values for  $c_p$ ,  $h$ , and  $s$ . Some properties of interest for aerothermodynamics are the internal energy, specific heat at constant volume, the ratio of specific heats, and the sonic velocity. These properties can be calculated from the following expressions:

$$\frac{u}{RT} = \frac{h}{RT} - 1 \quad (13)$$

$$\frac{c_v}{R} = \frac{c_p}{R} - 1 \quad (14)$$

$$\gamma = \frac{c_p}{c_p - R} \quad (15)$$

$$a = (\gamma RT)^{1/2} \quad (16)$$

In some computer codes it is necessary to know temperature as a function of enthalpy. This type of relation, in terms of logarithms, was determined by using a fourth degree polynomial curve fit of results from the statistical thermodynamic

relations. Over the temperature range of 100 K to 900 K, the temperature can be expressed as

$$\ln(T) = \sum_{n=1}^5 B_n [\ln(h)]^{n-1} \quad (17)$$

where

$$\left. \begin{aligned} B_1 &= -9.484043 \times 10^1 \\ B_2 &= 2.668556 \times 10^1 \\ B_3 &= -2.689611 \\ B_4 &= 1.204362 \times 10^{-1} \\ B_5 &= -1.949093 \times 10^{-3} \end{aligned} \right\} \quad (18)$$

The maximum temperature difference over the temperature range of 100 K to 900 K is 0.4° when compared with values from the statistical thermodynamic relations.

A less accurate curve fit for the temperature-enthalpy relation is

$$T = 0.08197 h^{0.6897} \quad (19)$$

This relation has a maximum difference of 2.6° over the temperature range of 220 K to 870 K when compared with values from the statistical thermodynamic relations.

While not as accurate as equation (17), this relation is useful in determining simple relations for the thermodynamic properties with sufficient accuracy for some analyses. Equation (19) can be inverted to yield

$$\frac{h}{R} = 0.3983 T^{1.4503} \quad (20)$$

and, then equation (20) can be differentiated to give

$$\frac{C_p}{R} = 0.5776 T^{0.4503} \quad (21)$$

Using equations (1), (11), and (20), the entropy can be expressed as

$$\frac{s}{R} = 26.42 + 1.283 T^{0.4503} - \ln(P) \quad (22)$$

The required constants of integration used in deriving equation (22) from equation (11) were taken from the statistical thermodynamic results. Over the temperature range of 260 K to 860 K, the values of  $c_p$ ,  $h$ , and  $s$  have maximum errors of 4.9, 1.0, and 0.52 percent, respectively, when compared with values from the statistical thermodynamic relations. While equations (20) to (22) are not as accurate as equations (7), (10), and (12) and are only valid over a narrower temperature range, they are of reasonable accuracy and within a temperature range to provide the properties for many studies. In the shocked region of flow over a model, the maximum temperature is only 800 K (limited by the tunnel stagnation temperature) and the lowest temperature will be approximately 300 K, the wall temperature of the model. Equation (19) can also be used with the equation of state, equation (1), to obtain

$$\frac{h}{R} = 5.435 \times 10^{-4} \left( \frac{P}{\rho} \right)^{1.4503} \quad (23)$$

The flow parameter and thermodynamic properties for the  $CF_4$  Tunnel are calculated by the thermodynamic relations from references 3 and 4. These reports use a difference reference state for enthalpy and entropy than used in the present report. The enthalpy and entropy based on the reference state used in the present report can be related to the values from the  $CF_4$  Tunnel by

$$\frac{h}{R} = \left( \frac{h}{R} \right)_t - 2076 \quad (24)$$

$$\frac{s}{R} = \left( \frac{s}{R} \right)_t + 0.15 \quad (25)$$

The subscript "t" refers to values from the CF<sub>4</sub> Tunnel.

#### TRANSPORT PROPERTIES

In the testing environment of the CF<sub>4</sub> Tunnel, the pressures are sufficiently low that high-pressure effects on the transport properties are negligible and the transport properties will only be a function of temperature. The relations used to predict the transport properties in the CF<sub>4</sub> Tunnel are taken from references 3 and 4 which use equations from reference 5 for the required transport properties at one atmosphere. The equations from reference 5 are based on a curve fit of experimental data over a temperature range of approximately 230 K to 460 K. In the present study, additional sources of experimental data were found from a literature search. Also, the kinetic theory of gases was used to interpret the experimental data and provide expressions for the transport properties of CF<sub>4</sub>.

#### Viscosity

The viscosity relation for CF<sub>4</sub> presented in reference 5 was determined by a curve fit of the experimental data taken from references 7 through 9 for a temperature range of 230 K to 460 K. This relation can be expressed as

$$\mu = \frac{1.5474 \times 10^{-6} T^{5/2}}{T^2 + 159.38 T - 5.3031} \quad (26)$$

The third term in the denominator is negligible and equation (26) can be written as

$$\mu = \frac{1.5474 \times 10^{-6} T^{3/2}}{T + 159.38} \quad (27)$$

which is of a Sutherland form for viscosity.

In the present study, additional sources of experimental data for the viscosity of  $\text{CF}_4$  were found from a literature search. The experimental data from references 7 through 21, which covers the temperature range of 150 K to 870 K, were used with the kinetic theory of gases to determine an expression for the viscosity of  $\text{CF}_4$ . From reference 22, the equation for the viscosity of a pure substance is

$$\mu = \frac{8.4411 \times 10^{-25} (\text{MT})^{1/2}}{\sigma^2 \Omega^{(2,2)}} \quad (28)$$

A Lennard-Jones (12-6) potential is used to calculate the reduced collision integral,  $\Omega^{(2,2)}$ , and, from reference 23, the reduced collision integral can be expressed as

$$\Omega^{(2,2)} = \frac{1.161145}{T^* (0.14874)} + \frac{0.52487}{\exp(0.77370T^*)} + \frac{2.16178}{\exp(2.43787T^*)} \quad (29)$$

where

$$T^* = \frac{T}{T_\epsilon} \quad (30)$$

in which  $T^*$  is the reduced temperature and  $T_\epsilon$  is the maximum energy of attraction expressed in temperature units. Equation (29) is a highly accurate formulation for the reduced collision integral and is valid over the range of  $T^*$  from 0.3 to 100. For the present study, an equation was curve fitted to values calculated from equation (29) to express the reduced collision integral as

$$\Omega^{(2,2)} = 0.7607 \left( 1 + \frac{1.094}{T^*} \right) \quad (31)$$

Equation (31) has a maximum error of  $\pm 0.5$  percent as compared with values from equation (29) over the range of  $T^*$  from 0.6 to 6 which is equivalent to a temperature range of 130 K to 990 K for the  $\text{CF}_4$  molecule.

Using equation (31) and the molecular weight for  $\text{CF}_4$ , equation (28) can be expressed as

$$\frac{2.5041 \times 10^{-25} T^{3/2}}{\mu} = 0.7607 \sigma^2 (T + 1.095 T_{\epsilon}) \quad (32)$$

The term on the lefthand side of equation (32) is a linear function of temperature and the experimental viscosity data can be easily used to determine values of  $\sigma$  and  $T_{\epsilon}$  for the  $\text{CF}_4$  gas. A plot of the experimental data from references 10 through 18 in the functional form of equation (32) is presented in figure 1. The functional form of equation (32) accurately represents the experimental data and yields

$$\sigma = 4.520 \times 10^{-10} \text{ m} \quad (33)$$

$$T_{\epsilon} = 165.5 \text{ K} \quad (34)$$

for the  $\text{CF}_4$  gas over the temperature range of 150 K to 870 K.

Using the values for  $\sigma$  and  $T_{\epsilon}$ , then the viscosity for the  $\text{CF}_4$  gas is given by

$$\mu = \frac{1.6112 \times 10^{-6} T^{3/2}}{T + 181.1} \quad (35)$$

Equation (35) is based on a Lennard-Jones (12-6) potential but also takes the Sutherland form for viscosity because of the use of equation (31) for the reduced collision integral. Equation (31) is only accurate for the temperature range of 132 K to 993 K for the  $\text{CF}_4$  molecule and for values of viscosity outside this

temperature range, then the basic equation for viscosity, equation (28), along with equation (29) for the reduced collision integral and the values for  $\sigma$  and  $T_E$  as given by equations (33) and (34) should be used. Equation (35) is highly accurate for use in the testing environment of the  $CF_4$  Tunnel.

A comparison of the experimental data with equations (35) and (27) is presented in figures 2 and 3. The comparison is presented in two figures for clarity because of the large number of experimental data points from 300 K to 500 K. As shown by the figures, equation (35) is in excellent agreement with the experimental data over the entire range of temperature. Results calculated with equation (27) deviate slightly from those in equation (35) at the extremities of the temperature range. A tabulation of the viscosities from the experimental data and from equation (35) and the percent differences between the two are presented in Table I. Over the temperature range of 150 K to 870 K, equation (35) should provide viscosity for gaseous  $CF_4$  at low pressures with differences of less than  $\pm 1$  percent when compared with the bulk of the experimental data. The maximum difference for any experimental data point is only 3.5 percent and these larger differences can be attributed to experimental accuracy.

#### Thermal Conductivity

The relation presented in reference 5 for the thermal conductivity of gaseous  $CF_4$  was based on the experimental data from references 24 through 26 which cover a temperature range of 270 K to 700 K. Due to differences in the temperature dependence between the sets of experimental data, the relation chosen by reference 5 was a linear curve fit of the experimental data from reference 24 which cover only the temperature range of 270 K to 410 K. The relation from reference 5 can be expressed as

$$k = 7.4051 \times 10^{-5} T - 6.2918 \times 10^{-3} \quad (36)$$



In the present study, additional sources of experimental data for the thermal conductivity for gaseous  $\text{CF}_4$  were found from a literature search. The experimental data from references 17 and 24 through 30, which cover the temperature range of 210 K to 700 K, were used in conjunction with kinetic theory to determine an expression for the thermal conductivity. While additional sources of experimental data were found, these sources did not greatly extend the temperature range or provide additional data in the temperature range of 410 K to 700 K. An accurate analysis for the thermal conductivity of gases is more difficult than for viscosity. The experimental data for thermal conductivity are, in general, not as accurate and the data from several sources not in as good agreement as the case for viscosity (see ref. 31). Furthermore, theoretical analysis from kinetic theory for polyatomic molecules require additional molecular and transport properties which are not readily available. Discussions on the theoretical methods for thermal conductivity of polyatomic molecules are presented in references 22, and 31 through 38.

The thermal conductivity of a polyatomic gas must account for the transport of translational and internal energy. The simplest analyses to begin with are the Eucken and modified Eucken formulations in which interactions between translational and internal energy are neglected. The modified Eucken formulation can be expressed as

$$\frac{k}{\mu} = \frac{15}{4} R + \frac{\rho D}{\mu} \left( c_p - \frac{5}{2} R \right) \quad (37)$$

where the first term on the RHS of the equation is due to the translational contribution and the second term is due to the internal contribution. The term  $\frac{\rho D}{\mu}$  is the reciprocal Schmidt number in which the diffusion coefficient  $D$  refers to the diffusive mechanism of internal energy. The Eucken formulation can be obtained by setting the Schmidt number equal to 1 in equation (37).

Generally, the experimental data will be between the values calculated by the Eucken and modified Eucken formulations. At low temperatures, where rotational energy is dominant, the experimental results will be closer to the Eucken formulation and then approach the modified Eucken formulation at higher temperatures. The diffusion coefficient for internal energy is not readily known for any gas; and, the value for this parameter is generally set equal to the self-diffusion coefficient. For a Lennard-Jones (12-6) potential the reciprocal Schmidt number has the value of 1.32 for the temperature range of interest in the present study. With this value for the reciprocal Schmidt number and the gas constant for  $\text{CF}_4$ , the modified Eucken formulation becomes

$$\frac{k}{\mu} = 1.32 c_p + 42.51 \quad (38)$$

and the Eucken formulation becomes

$$\frac{k}{\mu} = c_p + 118.1 \quad (39)$$

Using the expression for viscosity from equation (35) and the curve fit for  $c_p$  from equation (7), the thermal conductivity for gaseous  $\text{CF}_4$  can be calculated for the two Eucken formulations.

A comparison of the experimental data with the expression from reference 5, equation (36), and the Eucken formulation, equation (39), and the modified Eucken formulation, equation (38), from the present study is presented in figure 4. The experimental data are approximately 6-percent lower than the modified Eucken formulation and approximately 12-percent higher than the Eucken formulation. The linear curve fit of reference 5 agrees with the experimental data within approximately  $\pm 5$  percent.

A more rigorous treatment of the kinetic-theory approach to calculate thermal conductivity for polyatomic molecules which allows for inelastic collisions during

the translational-internal energy exchange during collisions is given in reference 34. This treatment showed that, in the first approximation, for quasi-elastic collisions, the modified Eucken formulation is obtained. However, in the second approximation, when inelastic collisions are considered the effect is a decrease in the contribution of translational energy to the thermal conductivity and an increase in the contribution by internal energy. The net result is a decrease in the thermal conductivity. The application of this rigorous treatment requires information, in addition to the diffusion coefficient for each internal energy state, on the relaxation time for exchange of energy between each internal state and translational energy. The relaxation time is commonly expressed as a collision number. Normally the vibrational collision number is an order of magnitude greater than the rotational collision number and the main contribution is the inelastic collision for the rotational-translational energy exchange.

Since the experimental data for  $\text{CF}_4$  are consistently slightly lower than values calculated from the modified Eucken formulation, the more rigorous kinetic-theory treatment which accounts for inelastic collisions was analyzed. The following analysis is based on the treatment given by reference 38. From equations (29) through (31) from reference 38, the thermal conductivity of a polyatomic molecule can be expressed as

$$\frac{k}{\mu} = \frac{5}{2} (c_v^t - \delta) + \frac{\rho D^r}{\mu} (c_v^r + \delta) + \frac{\rho D^v}{\mu} c_v^v \quad (40)$$

where

$$\delta = \frac{5}{\pi} \frac{c_v^r}{Z} \left[ 1 - \frac{2}{5} \left( \frac{\rho D^r}{\mu} \right) \right] \quad (41)$$

The translational and rotational contributions,  $c_v^t$  and  $c_v^r$ , to the specific heat for gaseous  $CF_4$  are each equal to  $3/2 R$  and the vibrational contribution can be expressed as

$$c_v^v = c_v - c_v^t - c_v^r \quad (42)$$

and, then using equation (14), the vibrational specific heat can be expressed as

$$c_v^v = c_p - 4R \quad (43)$$

The diffusion coefficients for the diffusion mechanism of the rotational and vibrational energies are approximated by the self-diffusion coefficient for a Lennard-Jones (12-6) potential. Thus,

$$\frac{\rho D^r}{\mu} = \frac{\rho D^v}{\mu} = 1.32 \quad (44)$$

Finally, using the gas constant for  $CF_4$ , the thermal conductivity for gaseous  $CF_4$  from equation (40) can be expressed as

$$\frac{k}{\mu} = 1.32 c_p + 42.51 - \frac{125.7}{Z} \quad (45)$$

This expression is the same as the modified Eucken formulation, equation (38), except for the correction term involving the rotational collision number.

Accurate values for the rotational collision number for  $CF_4$  are not available. Reference 28 presents a theoretical expression for the rotational collision number based on a rough-sphere model with an attractive potential well represented by the Lennard-Jones (12-6) potential. Using the present values from the viscosity analysis for the collision diameter and maximum energy of attraction, equations (33)

and (34), and the expression for the reduced collision integral, equation (31), the rotational collision number for  $\text{CF}_4$  based on the model of reference 28 becomes

$$Z = \frac{4.224 T + 764.6}{T \exp(165.5/T)} \quad (46)$$

This expression shows the rotational collision number to be an increasing function with temperature. Over the temperature range of 100 K to 900 K, the rotational collision number will increase from a value of approximately 2 to 4. There is no reason to believe that equation (46) is exactly correct for  $\text{CF}_4$  and the experimental data for the thermal conductivity are not sufficiently consistent between the different sources to use equation (45) to back out a rotational collision number to compare accurately with equation (46). A 1-percent error in the experimental data will give a change in  $Z$ , as calculated from equation (45), from 2 to 4.

In the present study, it is proposed to set the rotational collision number equal to a constant value of 2.97. Thus, from equation (45), the thermal conductivity for gaseous  $\text{CF}_4$  will become

$$\frac{k}{\mu} = 1.32 c_p \quad (47)$$

This choice will provide a simple expression for the thermal conductivity, slightly lower the values from that of the modified Eucken formulation, and roughly retain the features of the rigorous treatment for inelastic collisions.

A comparison of the experimental data for the thermal conductivity of  $\text{CF}_4$  with equation (47) is presented in figure 5. Also, a tabulation of the values of the thermal conductivity from the experimental data and from equation (47) and the percent differences between the two is presented in Table II. Equation (47) will go through the experimental data in the temperature range of 210 K to 430 K with a maximum difference of approximately  $\pm 5$  percent. The bulk of the experimental

data is in the temperature range of 300 K to 430 K and there are differences of 5 percent between the various sources. The only data at the higher temperatures are from reference 25. These data are not consistent with the other data in terms of trend with temperature and the data point at 335 K is much greater than the other experimental data. The accuracy of using equation (47) to calculate the thermal conductivity in the testing environment of the CF<sub>4</sub> Tunnel is comparable to the limited experimental data available. If one prefers a curve fit of the experimental data, then the expression from reference 5, as given by equation (36), is as good as any.

#### Prandtl Number

The Prandtl number is defined as

$$N_{Pr} = \frac{\mu c_p}{k} \quad (48)$$

and, from equation (47), the Prandtl number can be obtained as

$$N_{Pr} = 0.758 \quad (49)$$

#### RESULTS AND DISCUSSION

Equations are presented to calculate the thermodynamic properties of  $c_p$ ,  $h$ , and  $s$  as developed from three methods: (1) statistical thermodynamics (eqs. (3), (4), and (5)); (2) curve fit of  $c_p$  (eqs. (7), (10), and (12)); and (3) the temperature-enthalpy relation of equation (19) (eqs. (21), (20), and (22)). The selection of a particular set of equations will depend on application. A comparison of results from the three methods is presented in Table III. Also presented is a comparison of temperatures calculated from the two different temperature-enthalpy

relations given by equations (17) and (19) in which the values from the statistical thermodynamic method were used for enthalpy.

A tabulation of some thermodynamic and transport properties is presented in Table IV. The values for the thermodynamic properties are based on the curve-fit method (eqs. (7), (10), and (12)). The values for the transport properties are based on equations (35), (47), and (49).

The values tabulated in Tables III and IV cover the temperature range of 100 K to 900 K and are presented without regard to accuracies for the entire temperature range. The accuracy and applicable temperature range for each equation is presented in the sections entitled Thermodynamic Properties and Transport Properties.

#### CONCLUDING REMARKS

Relations for the thermodynamic and transport properties for gaseous  $\text{CF}_4$  are presented that can be used in flow-field computer codes and theoretical analyses for comparison of results with experimental data from the Langley Hypersonic  $\text{CF}_4$  Tunnel. These relations are valid at the low-pressure conditions which exist in the testing environment of the  $\text{CF}_4$  Tunnel and are simpler to use than the imperfect gas relations for thermodynamics and high-pressure relations for transport properties that are required and used to predict the complete flow from the reservoir to the test section.

In the present study, the thermodynamic properties of  $\text{CF}_4$  are based on a thermally-perfect, calorifically-imperfect gas. Relations are presented for the specific heat at constant pressure, enthalpy, and entropy in several forms for each property. Thus, a particular form can be selected that best fits the needs for a particular computer code or theoretical analysis.

The relations for the transport properties are based on the kinetic theory of gases in which published experimental data were used in the derivation of the relations and in defining the accuracy. As part of the present study, a literature

search was conducted and additional experimental data were located than had been previously used in development of relations for the transport properties in the  $\text{CF}_4$  Tunnel. Extensive experimental data were located for viscosity which covered the complete temperature range in the testing environment. Based on these data, the derived relation for viscosity should provide values with errors of less than 1 percent. The experimental data located for the thermal conductivity were limited with significant disagreement between the various sources and do not cover the complete temperature range of the testing environment. However, the available experimental data are in reasonable agreement with kinetic theory and the derived relation will probably provide values for the thermal conductivity with errors no more than 5 percent which is within the accuracy of the experimental data.



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TABLE I.- CF<sub>4</sub> VISCOSITY

T, K	$\mu, 10^{-5} \text{ N-s/m}^2$		Diff. Percent	Expt. Ref.
	Eq. (35)	Expt.		
150.0	.894	.923	3.25	14
160.0	.956	.978	2.30	14
180.0	1.078	1.091	1.25	14
200.0	1.196	1.205	.77	14
203.2	1.214	1.233	1.53	19
220.0	1.311	1.317	.47	14
223.2	1.329	1.356	2.04	19
234.5	1.392	1.420	2.00	9
240.0	1.423	1.427	.31	14
245.7	1.454	1.481	1.86	21
253.7	1.497	1.513	1.04	9
260.0	1.531	1.534	.17	14
273.2	1.602	1.623	1.34	19
274.0	1.606	1.616	.64	21
278.5	1.629	1.643	.84	9
280.0	1.637	1.639	.11	14
283.2	1.654	1.656	.13	21
288.8	1.683	1.707	1.44	9
293.0	1.704	1.706	.09	16
293.2	1.705	1.702	-.20	19
		1.701	-.26	21
		1.700	-.32	20
		1.735	1.18	15
295.0	1.715	1.726	.30	12
296.2	1.721	1.723	.04	13
296.5	1.722	1.731	-.00	11
298.2	1.731	1.731	-.00	10
		1.741	.05	14
300.0	1.740	1.756	.09	13
302.8	1.754	1.746	-.59	21
303.2	1.756	1.793	-.76	21
313.2	1.807	1.827	.73	7
314.6	1.814	1.840	-.03	14
320.0	1.841	1.860	.25	16
323.0	1.855	1.843	-.72	19
323.2	1.856	1.842	-.77	21
		1.864	.41	10
		1.915	.50	18
333.2	1.905	1.896	-.49	21
333.4	1.906	1.900	-.34	20
338.6	1.932	1.943	.59	7
339.2	1.935	1.950	.80	17
343.2	1.954	1.955	.06	21
348.0	1.977	1.988	.56	16
		1.992	.76	7

TABLE I.- Continued

T, K	$\mu, 10^{-5} \text{ N-s/m}^2$		Diff. Percent	Expt. Ref.
	Eq. (35)	Expt..		
353.5	2.003	2.000	-.16	20
363.2	2.049	2.050	.05	8
372.2	2.091	2.100	.43	12
373.0	2.095	2.105	.49	16
		2.090	-.23	20
373.2	2.096	2.111	.73	10
		2.114	.88	11
		2.111	.73	18
374.4	2.101	2.124	1.08	7
393.1	2.187	2.180	-.32	20
393.2	2.187	2.192	.21	8
		2.170	-.80	19
394.0	2.191	2.206	.68	15
397.6	2.207	2.212	.21	7
400.0	2.218	2.230	.53	16
403.0	2.232	2.243	.51	16
413.1	2.277	2.285	.37	7
413.2	2.277	2.260	-.75	20
421.9	2.316	2.345	1.27	7
423.0	2.320	2.333	.55	16
423.2	2.321	2.327	.25	10
		2.346	1.07	18
		2.319	-.10	8
431.9	2.359	2.367	.33	7
432.8	2.363	2.340	-.98	20
433.2	2.365	2.324	-1.73	19
448.2	2.429	2.398	-1.29	7
450.0	2.437	2.458	.86	16
455.7	2.461	2.436	-1.03	7
468.2	2.514	2.521	.28	10
		2.519	.20	18
473.0	2.534	2.549	.59	16
473.2	2.535	2.540	.21	11
		2.477	-2.28	19
477.2	2.551	2.568	.65	12
498.0	2.637	2.640	.13	16
523.0	2.737	2.737	.00	16
528.2	2.758	2.765	.27	10
547.0	2.831	2.845	.49	15
566.0	2.904	2.904	.00	16
573.0	2.931	2.926	-.16	16
573.2	2.931	2.939	.26	10
		2.935	.13	11

TABLE I.- Concluded

T, K	$\mu, 10^{-5} \text{ N-s/m}^2$		Diff. Percent	Expt. Ref.
	Eq. (35)	Expt..		
623.0	3.116	3.107	-.28	16
668.2	3.277	3.277	.01	11
673.0	3.294	3.274	-.59	16
698.0	3.380	3.386	.18	15
723.0	3.464	3.441	-.68	16
768.2	3.614	3.617	.09	10
773.0	3.629	3.601	-.78	16
803.0	3.725	3.699	-.71	16
823.0	3.789	3.738	-1.33	16
873.0	3.943	3.939	-.09	15
		3.807	-3.44	16
873.2	3.943	3.943	-.01	10

TABLE II.- CF<sub>4</sub> THERMAL CONDUCTIVITY

T, K	k, 10 <sup>-2</sup> w/m-K		Diff. Percent	Expt. Ref.
	Eq. (47)	Expt.		
213.2	.939	.990	5.43	27
233.2	1.082	1.140	5.33	27
253.2	1.232	1.290	4.72	27
273.2	1.386	1.440	3.87	27
277.4	1.419	1.400	-1.35	24
288.0	1.503	1.497	-.40	28
293.2	1.544	1.590	2.95	27
299.0	1.591	1.566	-1.56	24
300.0	1.599	1.580	-1.18	29
300.0	1.599	1.680	5.08	30
309.3	1.674	1.640	-2.01	24
313.2	1.705	1.740	2.05	27
331.9	1.857	1.809	-2.58	24
333.2	1.867	1.870	.14	27
335.0	1.882	2.070	9.98	25
336.0	1.890	1.840	-2.66	26
339.2	1.916	1.900	-.85	17
353.2	2.030	2.040	.47	27
353.6	2.034	1.978	-2.74	24
371.9	2.183	2.120	-2.88	26
373.2	2.194	2.180	-.62	27
374.7	2.206	2.138	-3.07	24
385.7	2.295	2.215	-3.49	24
393.2	2.356	2.330	-1.11	27
401.6	2.424	2.350	-3.05	26
407.4	2.471	2.375	-3.88	24
413.2	2.518	2.480	-1.49	27
433.2	2.678	2.630	-1.78	27
434.1	2.685	2.480	-7.63	26
474.9	3.006	3.000	-.21	25
527.7	3.411	3.280	-3.84	25
571.1	3.733	3.590	-3.84	25
620.7	4.091	3.860	-5.65	25
674.2	4.462	4.210	-5.66	25
698.2	4.623	4.340	-6.13	25

TABLE III.- COMPARISON OF THERMODYNAMIC PROPERTIES

T, K	$c_p/R$		$h/RT$				$s/R^*$		$T_c, K$		
	Eq. (3)	Eq. (7)	Eq. (21)	Eq. (4)	Eq. (10)	Eq. (20)	Eq. (5)	Eq. (12)	Eq. (22)	Eq. (17)	Eq. (19)
100.0	4.18	4.15	4.59	4.027	4.027	3.168	25.53	25.53	25.10	99.9	118.0
120.0	4.39	4.40	4.99	4.069	4.068	3.439	26.31	26.31	25.97	120.2	134.7
140.0	4.67	4.69	5.35	4.134	4.136	3.686	27.00	27.01	26.77	140.2	151.5
160.0	4.99	5.01	5.68	4.221	4.225	3.915	27.65	27.65	27.50	160.1	168.5
180.0	5.34	5.34	5.99	4.326	4.330	4.128	28.25	28.26	28.19	179.9	185.9
200.0	5.70	5.69	6.28	4.445	4.449	4.329	28.84	28.84	28.84	199.9	203.7
220.0	6.05	6.04	6.55	4.575	4.578	4.519	29.39	29.40	29.45	219.8	221.8
240.0	6.40	6.38	6.81	4.712	4.714	4.699	29.94	29.94	30.03	239.8	240.4
260.0	6.74	6.72	7.06	4.855	4.855	4.872	30.46	30.47	30.59	259.9	259.4
280.0	7.06	7.05	7.30	5.001	5.000	5.037	30.97	30.98	31.12	279.9	278.6
300.0	7.37	7.37	7.53	5.149	5.148	5.196	31.47	31.47	31.63	300.0	298.1
320.0	7.67	7.67	7.76	5.297	5.296	5.349	31.96	31.96	32.12	320.0	317.8
340.0	7.95	7.95	7.97	5.445	5.444	5.497	32.43	32.43	32.60	340.1	337.7
360.0	8.22	8.22	8.18	5.591	5.591	5.640	32.89	32.90	33.06	360.1	357.8
380.0	8.47	8.48	8.38	5.736	5.736	5.779	33.34	33.35	33.51	380.1	378.0
400.0	8.71	8.72	8.58	5.879	5.879	5.914	33.78	33.79	33.95	400.1	398.3
420.0	8.93	8.94	8.77	6.019	6.020	6.046	34.21	34.22	34.37	420.2	418.6
440.0	9.14	9.15	8.95	6.156	6.157	6.174	34.63	34.64	34.78	440.1	439.1
460.0	9.34	9.35	9.13	6.290	6.292	6.299	35.04	35.05	35.18	460.1	459.5
480.0	9.53	9.53	9.31	6.421	6.423	6.421	35.45	35.45	35.58	480.1	480.0
500.0	9.71	9.70	9.48	6.549	6.551	6.540	35.84	35.84	35.96	500.1	500.4

\*For  $p = 101325 \text{ N/m}^2$



TABLE III.- Concluded

T, K	$c_p/R$		$h/RT$				$s/R^*$		$T_c, K$		
	Eq. (3)	Eq. (7)	Eq. (21)	Eq. (4)	Eq. (10)	Eq. (20)	Eq. (5)	Eq. (12)	Eq. (22)	Eq. (17)	Eq. (19)
520.0	9.87	9.87	9.65	6.674	6.675	6.656	36.22	36.23	36.33	520.1	520.9
540.0	10.03	10.02	9.82	6.795	6.796	6.770	36.60	36.60	36.70	540.0	541.3
560.0	10.17	10.16	9.98	6.913	6.914	6.882	36.97	36.97	37.06	560.0	561.7
580.0	10.31	10.30	10.14	7.028	7.028	6.992	37.32	37.33	37.42	580.0	582.0
600.0	10.44	10.43	10.30	7.140	7.140	7.099	37.68	37.68	37.76	599.9	602.3
620.0	10.56	10.55	10.45	7.248	7.248	7.205	38.02	38.03	38.10	619.9	622.5
640.0	10.67	10.67	10.60	7.353	7.353	7.309	38.36	38.36	38.44	639.9	642.6
660.0	10.78	10.78	10.75	7.455	7.455	7.411	38.69	38.69	38.76	659.9	662.6
680.0	10.88	10.88	10.89	7.555	7.554	7.511	39.01	39.02	39.09	679.8	682.6
700.0	10.97	10.98	11.04	7.651	7.651	7.610	39.33	39.33	39.41	699.8	702.5
720.0	11.06	11.06	11.18	7.744	7.744	7.707	39.64	39.64	39.72	719.8	722.3
740.0	11.14	11.15	11.31	7.835	7.835	7.802	39.94	39.95	40.03	739.9	742.0
760.0	11.22	11.22	11.45	7.923	7.923	7.897	40.24	40.25	40.33	759.9	761.6
780.0	11.29	11.29	11.59	8.008	8.009	7.990	40.53	40.54	40.63	779.9	781.1
800.0	11.36	11.36	11.72	8.091	8.092	8.081	40.82	40.82	40.92	800.0	800.6
820.0	11.43	11.42	11.85	8.172	8.172	8.171	41.10	41.11	41.22	820.0	819.9
840.0	11.49	11.48	11.98	8.250	8.250	8.261	41.38	41.38	41.50	840.1	839.1
860.0	11.55	11.54	12.11	8.326	8.326	8.349	41.65	41.65	41.79	860.2	858.3
880.0	11.60	11.60	12.23	8.400	8.400	8.436	41.91	41.92	42.07	880.3	877.3
900.0	11.66	11.67	12.36	8.472	8.472	8.521	42.18	42.18	42.34	900.4	896.3

\*For  $p = 101325 \text{ N/m}^2$

TABLE IV.- THERMODYNAMIC AND TRANSPORT PROPERTIES

T K	$c_p/R$	$h/RT$	$s/R^*$	$\gamma$	a m/s	$\mu$ $10^{-5} \text{ N-s/m}^2$	k $10^{-2} \text{ W/m-K}$	$N_{Pr}$
100.0	4.15	4.027	25.53	1.317	111.5	.573	.297	.758
120.0	4.40	4.068	26.31	1.294	121.1	.703	.386	.758
140.0	4.69	4.136	27.01	1.271	129.7	.831	.486	.758
160.0	5.01	4.225	27.65	1.250	137.4	.956	.597	.758
180.0	5.34	4.330	28.26	1.230	144.6	1.078	.718	.758
200.0	5.69	4.449	28.84	1.213	151.4	1.196	.848	.758
220.0	6.04	4.578	29.40	1.199	157.8	1.311	.987	.758
240.0	6.38	4.714	29.94	1.186	164.0	1.423	1.133	.758
260.0	6.72	4.855	30.47	1.175	169.9	1.531	1.284	.758
280.0	7.05	5.000	30.98	1.165	175.6	1.637	1.440	.758
300.0	7.37	5.148	31.47	1.157	181.1	1.740	1.599	.758
320.0	7.67	5.296	31.96	1.150	186.5	1.841	1.760	.758
340.0	7.95	5.444	32.43	1.144	191.7	1.938	1.923	.758
360.0	8.22	5.591	32.90	1.138	196.8	2.034	2.086	.758
380.0	8.48	5.736	33.35	1.134	201.7	2.127	2.249	.758
400.0	8.72	5.879	33.79	1.130	206.6	2.218	2.411	.758
420.0	8.94	6.020	34.22	1.126	211.4	2.307	2.572	.758
440.0	9.15	6.157	34.64	1.123	216.0	2.394	2.732	.758
460.0	9.35	6.292	35.05	1.120	220.6	2.479	2.890	.758
480.0	9.53	6.423	35.45	1.117	225.1	2.563	3.046	.758
500.0	9.70	6.551	35.84	1.115	229.5	2.645	3.200	.758

TABLE IV.- Concluded

T K	$c_p/R$	$h/RT$	$s/R^*$	$\gamma$	a m/s	$\mu$ $10^{-5} \text{ N-s/m}^2$	$k$ $10^{-2} \text{ w/m-k}$	$N_{Pr}$
520.0	9.87	6.675	36.23	1.113	233.8	2.725	3.353	.758
540.0	10.02	6.796	36.60	1.111	238.1	2.804	3.503	.758
560.0	10.16	6.914	36.97	1.109	242.2	2.881	3.652	.758
580.0	10.30	7.028	37.33	1.108	246.3	2.957	3.799	.758
600.0	10.43	7.140	37.68	1.106	250.4	3.032	3.943	.758
620.0	10.55	7.248	38.03	1.105	254.4	3.105	4.086	.758
640.0	10.67	7.353	38.36	1.103	258.3	3.177	4.227	.758
660.0	10.78	7.455	38.69	1.102	262.2	3.248	4.365	.758
680.0	10.88	7.554	39.02	1.101	266.0	3.318	4.502	.758
700.0	10.98	7.651	39.33	1.100	269.7	3.387	4.635	.758
720.0	11.06	7.744	39.64	1.099	273.5	3.454	4.767	.758
740.0	11.15	7.835	39.95	1.099	277.1	3.521	4.895	.758
760.0	11.22	7.923	40.25	1.098	280.8	3.587	5.021	.758
780.0	11.29	8.009	40.54	1.097	284.3	3.652	5.144	.758
800.0	11.36	8.092	40.82	1.097	287.9	3.716	5.264	.758
820.0	11.42	8.172	41.11	1.096	291.4	3.779	5.383	.758
840.0	11.48	8.250	41.38	1.095	294.8	3.841	5.500	.758
860.0	11.54	8.326	41.65	1.095	298.3	3.903	5.616	.758
880.0	11.60	8.400	41.92	1.094	301.6	3.964	5.734	.758
900.0	11.67	8.472	42.18	1.094	305.0	4.024	5.854	.758

\*For  $p = 101325 \text{ N/m}^2$



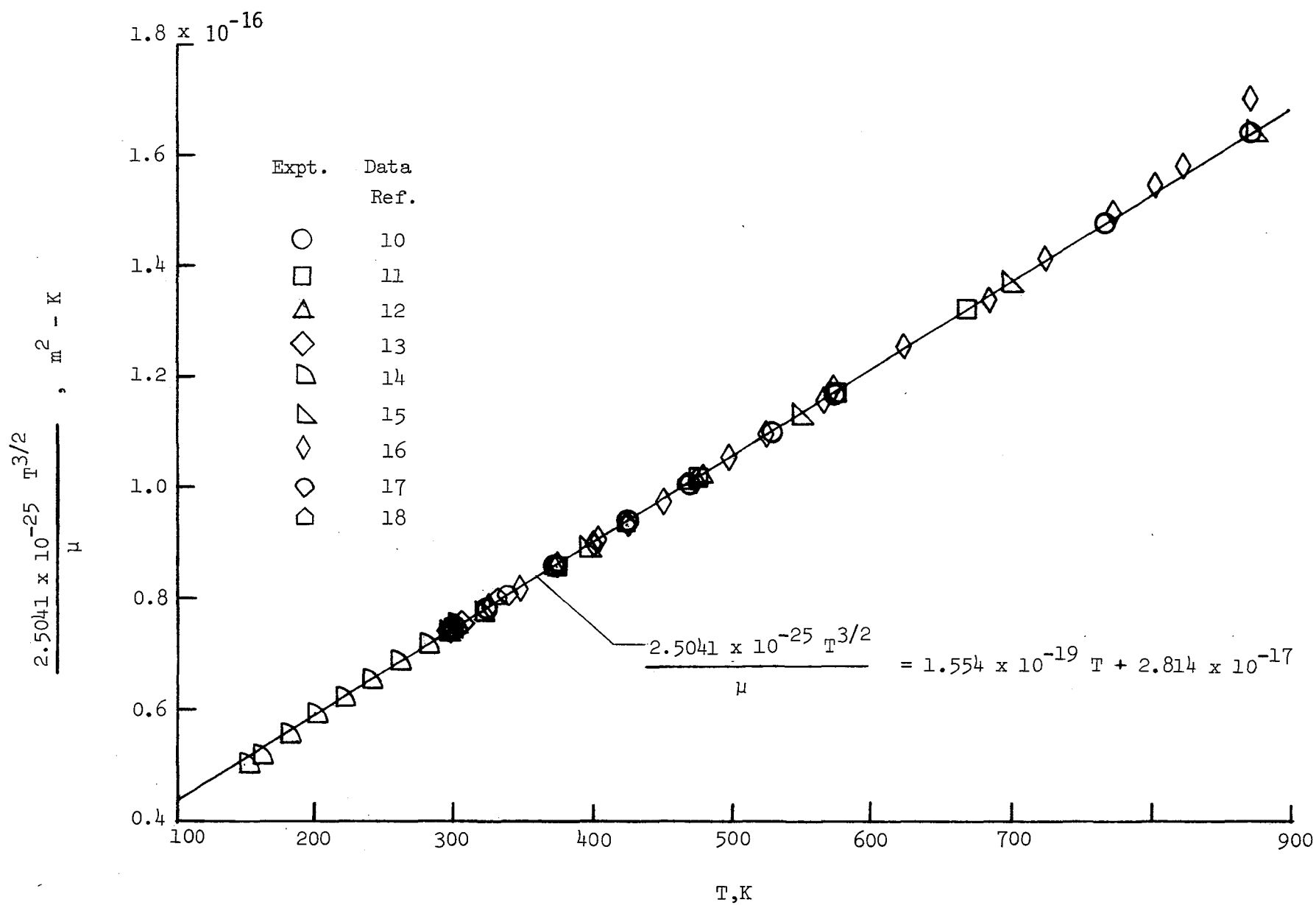


Figure 1. - Viscosity relation used to determine values of  $\sigma$  and  $T_{\epsilon}$  for  $\text{CF}_4$ .

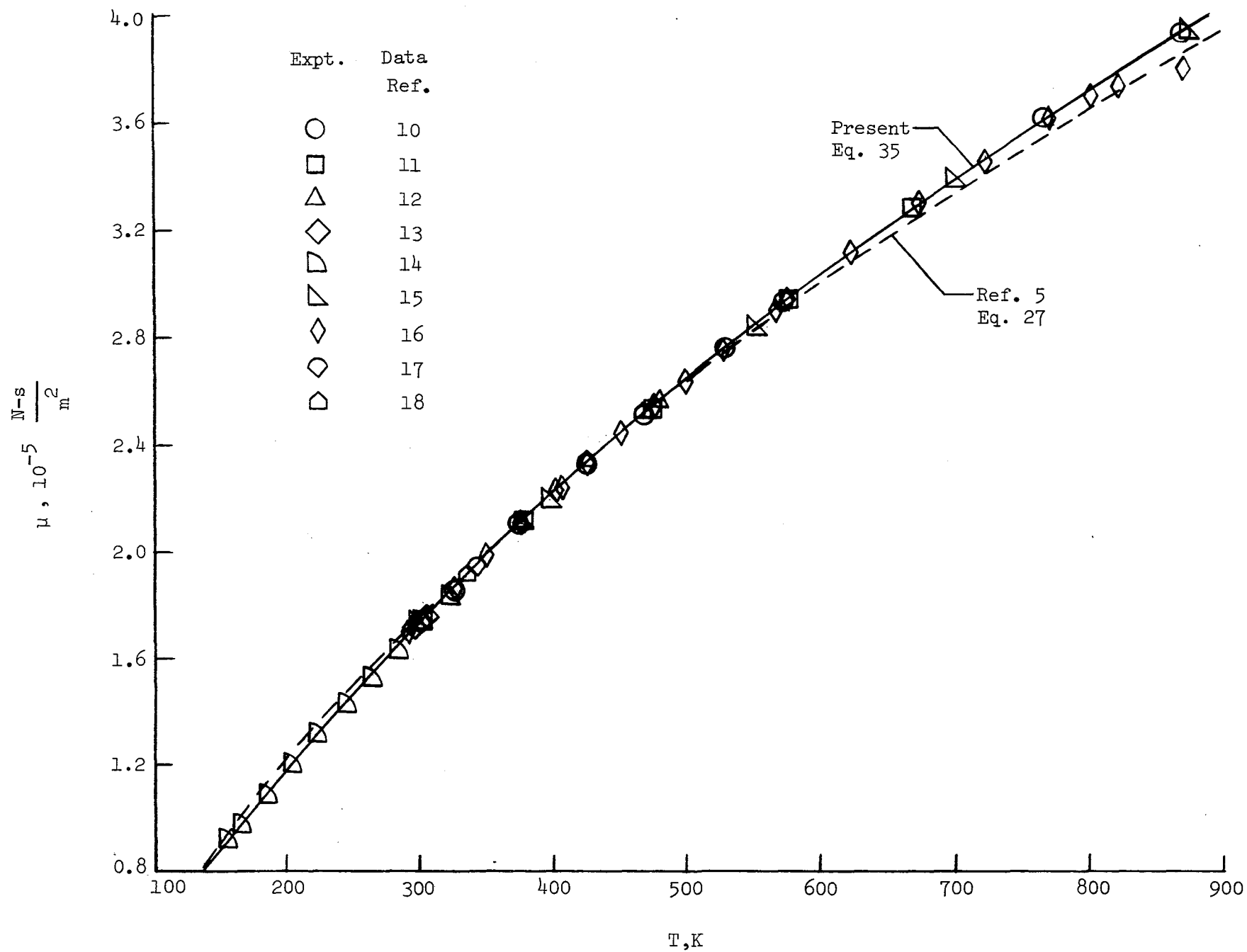


Figure 2. - Comparison of equation for  $\text{CF}_4$  viscosity with experimental data from references 10 through 18.

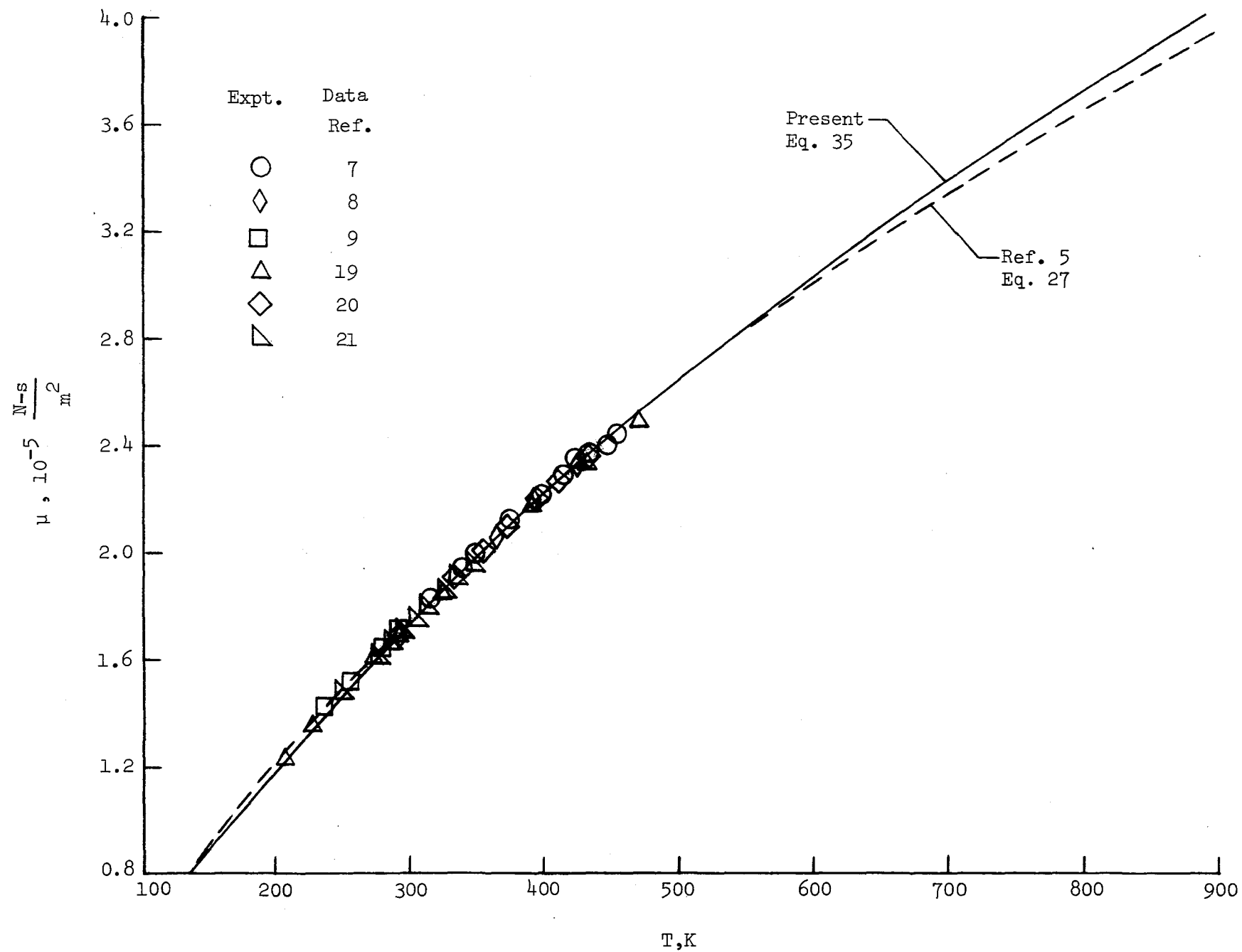


Figure 3. - Comparison of equations for  $\text{CF}_4$  viscosity with experimental data from references 7 through 9 and 19 through 21.

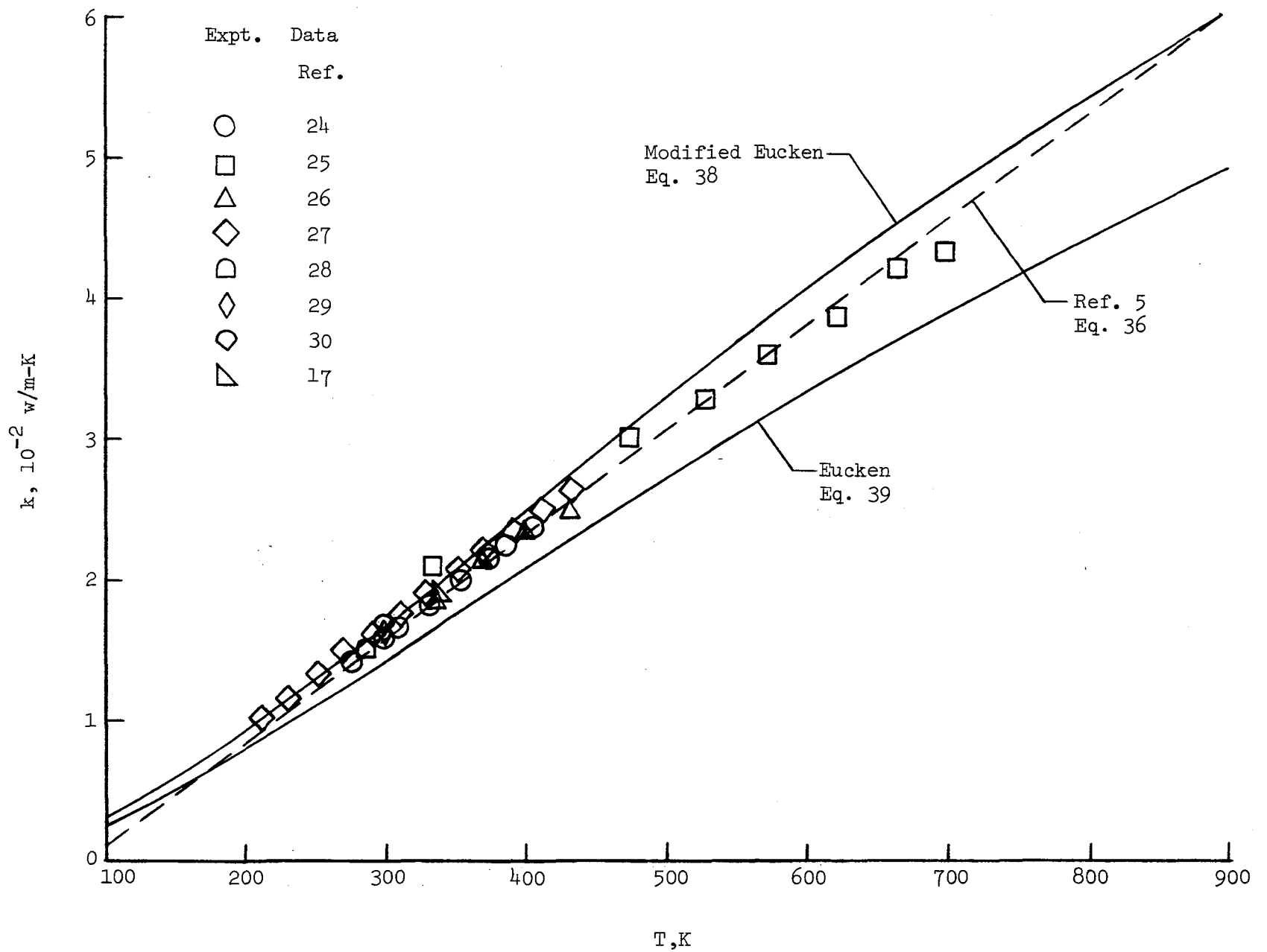


Figure 4. - Comparison of equations for  $\text{CF}_4$  thermal conductivity with experimental data.



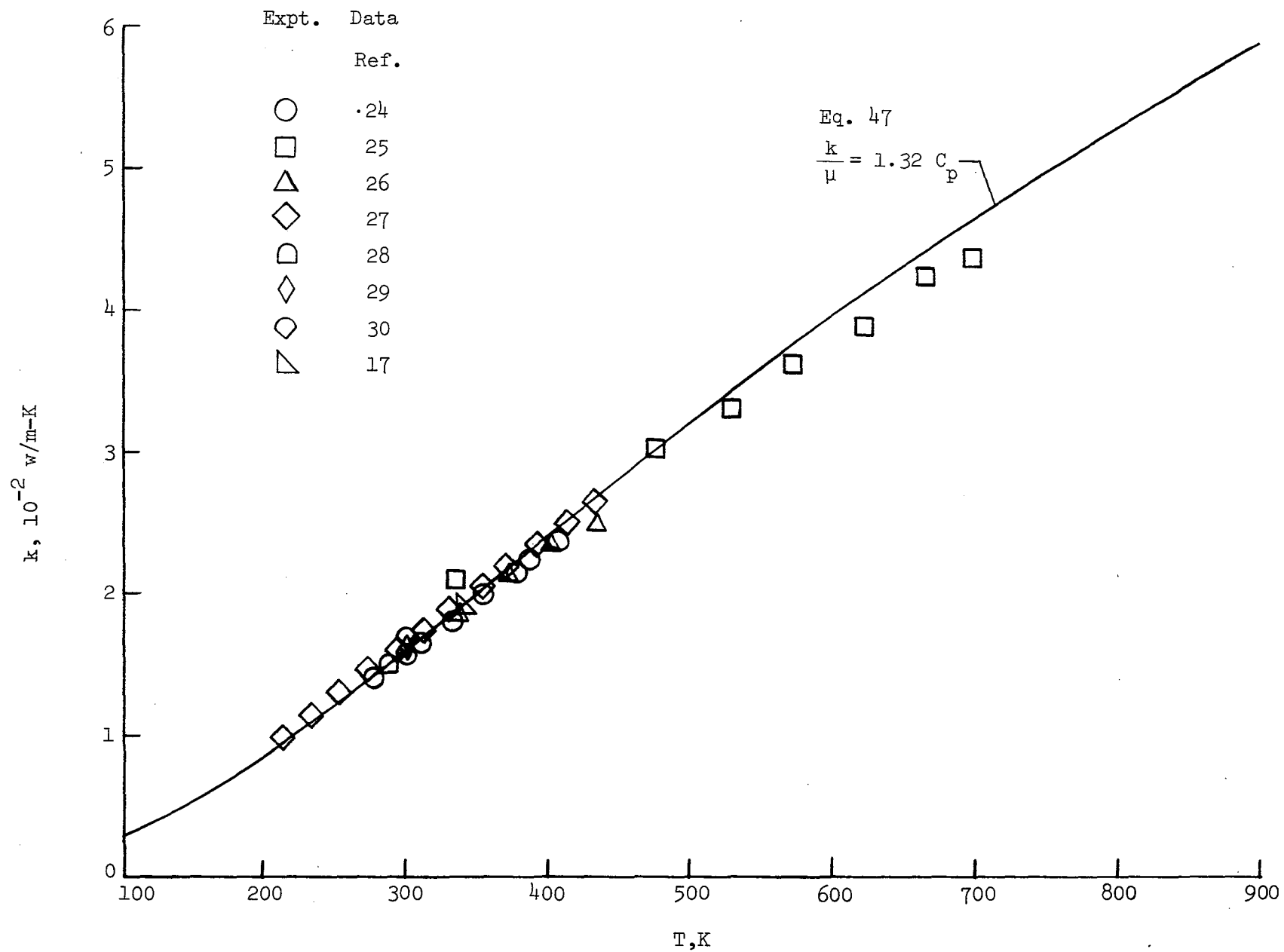


Figure 5. - Comparison of equation 47 for  $\text{CF}_4$  thermal conductivity with experimental data.



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16. Abstract <p>Relations for the thermodynamic and transport properties for gaseous CF<sub>4</sub> are presented that can be used in flow-field computer codes and theoretical analyses for comparison of results with experimental data from the Langley Hypersonic CF<sub>4</sub> Tunnel. The thermodynamic relations are based on a thermally perfect but calorifically imperfect gas. These relations are adequate for the testing environment of the CF<sub>4</sub> Tunnel and are simpler to use than the imperfect gas relations required to define the complete expansion from the tunnel reservoir.</p> <p>The relations for the transport properties are based on the kinetic theory of gases in which published experimental data are used in the derivation of the relations. Extensive experimental data were located for viscosity and the derived relation should provide values for viscosity with errors of less than 1 percent. The experimental data for thermal conductivity were limited with significant disagreement between the various sources. Based on the limited experimental data, the derived relation will probably provide values for the thermal conductivity with errors of no more than 5 percent which is within the accuracy of the experimental data.</p>					
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